AD-A123·868 ELECTRODEPOSITION OF REFRACTORY CARBIDE COATINGS(U)
NAVAL RESEARCH LAB WASHINGTON DC   K H STERN 30 DEC 82   1/
NRL-MR-4995 SBI-AD-E000 522

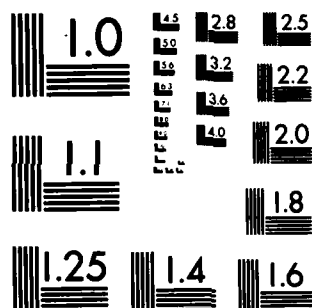UNCLASSIFIED   F/G 7/1   NL

END
DATE
FILMED
83
DTIC

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 4995	2. GOVT ACCESSION NO. AD-A 123 868	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRODEPOSITION OF REFRACTORY CARBIDE COATINGS		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. H. Stern		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62543; SF43-400-391; 61-0024-0-3
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE December 30, 1982
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Carbides
Electrodeposition
Molden salts

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A novel method for electrodepositing refractory carbide coatings from molten salts is described. It consists of the simultaneous reduction of the appropriate metal species dissolved in the ternary LiF-NaF-KF eutectic and carbonate dissolved in the same melt. The metal and carbon deposit on the cathode where they react to form the carbide. The coatings are hard, abrasion resistant, and resist oxidation in air to 500°C. Carbides of tantalum and tungsten have been plated so far, and the method is applicable to other carbides as well.

DD $_{1 \text{ JAN } 73}^{\text{FORM}}$ 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

Electrodeposition of Refractory Carbide Coatings

Ever since the first iron weapon demolished one of bronze, man has recognized the advantages which greater hardness in metals offered. Hardness of metals was significant in more peaceful pursuits as well, for harder metals, more resistant to wear, could reduce the need for frequent, costly replacement of parts.

Modern technology, a long way from the bronze or iron age, still contends with this unsolved problem, although it now appears in more sophisticated forms. For several years the American Chemical Society has sponsored National Symposia on Wear and Corrosion at which these continuing problems are addressed. Abrasive wear afflicts all manner of machinery in which metal surfaces contact other surfaces, whether these be mineral, as in mining and grinding operations, or other metal surfaces. Erosive wear plagues metals exposed to high velocity gas streams carrying hard particles, as in coal gasification, or even the lower velocity, liquid-entrained coal particles in a slurry flowing through a pipeline. These problems of wear are

1

frequently aggravated by high temperatures which lead to simultaneous metal oxidation, particularly in the newer energy industries.

Attempts to reduce wear are probably as old as the problems they address. Chief among these is the formulation of ever harder alloys, such as the newer ones based on cobalt. Another route is to modify only surface properties, rather than the bulk of the metal. This can be done by covering the bulk metal with a coating of another alloy. Still another method is to modify the surface layer of the metal either by diffusing other metals into the surface (metalliding)(1), by ion implantation, or by laser melting.

It has long been recognized that refractory carbides possess precisely the desirable hardness missing from metals, but lack the desirable ductility of metals. Consequently there have been many attempts to combine the two in order to gain hardness combined with ductility. One well-known technique is hard-facing, the incorporation of carbide particles into a bulk metal. Another is to produce carbide coatings on metals. However, existing coating methods have not been entirely successful. Plasma spraying, which involves impinging the carbide powder on the surface to be coated, requires temperatures near 1500°C, is line-of-sight, and tends to produce somewhat porous coatings.
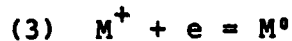
Chemical vapor deposition can be carried out by combining
two reactive gases so that the carbide reaction product is
produced as a coating. Much development work has been done
on this process (2), but the coatings are usually quite
thin.

A method frequently mentioned for the preparation of
carbides (3) is electrochemical reduction. The reference is
invariably an article by Weiss (4) which reports work done
in France during World War II. This remarkable paper, over
fifty pages long, describes in great detail the electro-
chemical preparation of binary compounds--carbides, borides,
arsenides--of tungsten a d molybdenum. In these experiments
carbides were deposited from melts containing alkali metal
fluorides and B_2O_3; the metal and carbon were introduced as
the oxide and as carbonate, respectively. Electrolysis
resulted in the formation of millimeter-size crystals on the
walls of the graphite crucible which served as the cathode.
Analysis of the crystals showed that their composition
varied with the metal oxide/carbonate ratio in the melt. On
reading this paper it seemed fairly obvious that the only
function of the B_2O_3 was to solubilize the oxide, and that
it would be easier, since B_2O_3 is difficult to dry, to add
the metal in soluble form. This had in fact already been
done by Senderoff and Mellors (5) in an extensive research
program carried out at Union Carbide during the 1960's.

They showed that excellent coatings of the refractory metals could be electroplated from the ternary eutectic of (Li, Na, K)F by adding the metal as a complex fluoride, and plating between the appropriate metal anode and the cathode to be plated at 750-800°C. Dense, adherent, and ductile plates were obtained, and there seemed to be no upper limit to the plating thickness; in fact the substrate could be dissolved away to produce free-standing refractory metal objects. However, the inventors pointed out that not only halides other than fluoride, but also oxyanions, must be absent for the process to be satisfactory.

On the basis of this previous work it seemed that refractory carbide coatings might be electrodeposited if (1) the reduction of carbonate (an oxyanion) did not interfere with the reduction of the metal and (2) if the metal and carbon would react at 800°, since the elements in bulk typically react only near 1400°. Moreover, carbon is not the only possible product of carbonate reduction. For pure alkali metal carbonates four reactions are possible[6]:

$$(1) \quad CO_3^{2-} + 4e = C + 3O^{2-}$$

$$(2) \quad CO_3^{2-} + 2e = CO + 2O^{2-}$$

4

(3) $M^+ + e = M^0$

(4) $2CO_3^{2-} + 10e = C_2^{2-} + 6O^{2-}$

Which reaction is favored depends on both the cation and the temperature. For carbide formation to occur, reaction (1) is required. It was not known whether this reaction would be favored in the ternary fluoride melt. An additional complication is that the anodic reaction in all cases is

$$CO_3^{2-} = CO_2 + 1/2O_2 + 2e$$

This might interfere with dissolution of the anode which also serves as the source of the metal, and by contamination of the reactor atmosphere with oxygen, which must be excluded for good metal deposition.

The first experiments were directed toward tantalum carbide formation. This material had never previously been electrodeposited, but a soluble form, $K_2Ta_2F_7$, was commercially available as a source of tantalum in the fluoride melt. Nickel is suitable as container material for the fluoride melts which attack even Inconel. The alkali metal fluorides were vacuum dried and the solvent purified by pre-electrolysis between graphite electrodes. All

5

operations were carried out in a large reactor which could

be evacuated or filled with argon. As expected on the basis

of previous work (5), tantalum was plated on the nickel

cathodes. The next problem was to establish which

parameters determined carbide formation. If one assumes

100% current efficiency for the two processes:

$$Ta^{5+} + 5e = Ta^0$$

$$CO_3^{2-} + 4e = C + 3O^{2-}$$
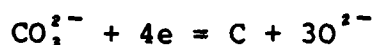
one might expect approximately equal molar concentrations of

TaF_7^{2-} and CO_3^{2-} to be required to plate TaC, but matters were

not that simple. After considerable work, it was determined

that the deposition voltage and, at constant tantalum

concentration, the carbonate concentration determined the

composition of the coating. The result was a map, as shown

in figure 1, which gives the coating composition (identified

by X-ray diffraction of the surface) as a function of

deposition voltage and carbonate concentration. Multiple

symbols indicate that both TaC and Ta₂C were plated in a

single experiment, or that experiments under nominally the

same conditions give different compositons. So far, current

efficiencies up to 50% have been achieved. The nature of

the coating is shown in figure 2. It consists of fine

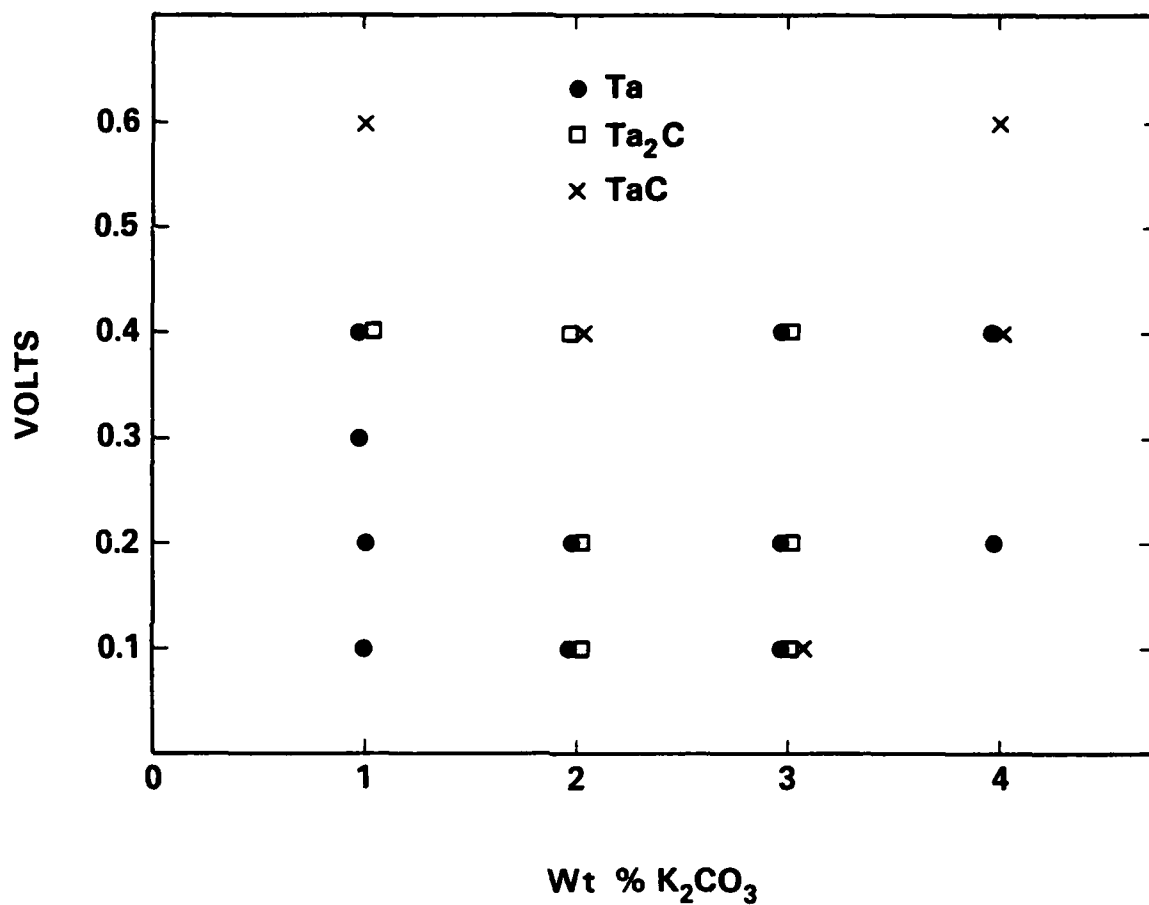crystals in the micron range. The darker zone evident in

Fig. 1 Dependence of coating composition on voltage and carbonate concentration in the melt (at constant tantalum concentration).

7

Fig. 2 Electron micrograph of tantalum carbide coating; upper
picture--top view; lower picture--cross section. Tungsten carbide
coatings appear similar.

the cross-section contains both nickel and tantalum, and is probably formed by interdiffusion between the coating and the substrate. Oxidation tests show that the coatings are stable in ambient air up to 500°C. Preliminary hardness tests give Knoop hardness numbers in the 1000-1500 range, and the abrasion resistance is excellent.

The next study was concerned with tungsten carbide coatings. In their original work Senderoff and Mellors (5) had found that a tungsten valence of +4.5 was required for tungsten plating. They achieved this be reacting WF_6, a gas, with tungsten powder dispersed in the melt. This procedure seemed too difficult for a practical process, and Na_2WO_4 was therefore tried as solute, although it contains an oxyanion. Tungsten plated satisfactorily and the combination with carbonate reduction led to tungsten carbide coatings of a quality and appearance similar to that of the tantalum carbide, except that the interdiffusion zone was absent. Over a wide variety of conditions only W_2C was produced. When WC was formed, it was frequently with current efficiencies of less than 10%.

Now that tantalum and tungsten carbides have been successfully plated, the question is--what next? Research opportunities exist in several areas:

(1) Other Carbides

Each carbide has specific properties which might make it the coating of choice for a particular application. Therefore it would be useful to know how to prepare other carbide coatings beside the two already done. For example, one would expect chromium carbide to have superior oxidation resistance. However, each carbide synthesis, in addition to common features, also possesses unique aspects. Thus, even if we know how to plate the metal and carbon, it is not certain that they will react on the cathode at a reasonable temperature. Each synthesis is a problem to be worked out.

(2) Substrates

Although we have plated carbides on nickel substrates, both because it is a representative metal and because it is not corroded by the melt, we don't know the plating characteristics on other metals which it might be desirable to plate.

(3) Mechanism

High on our list of priorities is to elucidate the mechanism of the plating process, as an electrode kineticist understands that term. We are dealing with two simultaneous reductions (metal and carbon) on a single cathode, each requiring several electrons, with a subsequent chemical reaction on the surface. Multi-electron reactions usually do not occur in a single step. One might expect that different steps of the mechanism would be differently affected by concentration and voltage. An examination of carbon-metal phase diagrams shows that they are all quite complicated, exhibiting not only several stoichiometric compounds (e.g. WC, W_2C), but also large composition regions where defect structures exist. The control of coating composition therefore probably depends directly on understanding the mechanism, i.e., the knowledge of all the individual steps and their rates. In turn, coating properties most likely depend directly on coating composition.

(4) Coating Microstructure

Our knowledge of coating composition so far depends on X-ray diffraction of the coating, and comparison of the diffraction peaks with the powder patterns of known

carbides. This technique averages the composition over a fairly wide area and depth. We expect to apply the more modern techniques of surface analysis, such as ion microprobe and Auger, to determine coating composition on a finer scale as well as a function of depth. A preliminary look at the tantalum carbide cross-section (fig. 2) by these means showed that the dark zone next to the substrate contains both nickel and tantalum, and that the concentration profiles of these elements is consistent with interdiffusion. Studies of this type should give us a better view of coating structure, and hence lead to better coatings.

(5) Mechanical Properties and Oxidation Resistance

Since the major reason for using carbides is their great hardness, further studies of hardness, abrasion resistance, and friction are required. Although preliminary tests on selected coatings look very promising, we do not yet know the relation between these properties and the coating composition. Thus a knowledge of the mechanism which will lead to better control of the coating composition should have a direct impact on optimizing mechanical properties for particular applications. The same argument applies to coating composition.

(6) Complex Shapes

One of the major advantages of electrodeposition is the ability to coat complex shapes. For practical applications the spatial arrangements of anode and cathode must be carefully worked out. At this stage of our research program we have not concentrated on this aspect, although we have plated the inside and outside of a short cylinder with our research cell which was designed for plating flat coupons. The process appears easily adaptable for plating complex shapes.

It should be evident from the above description that carbide electrodeposition is a highly useful technique which should be applicable in a wide variety of technologies where wear is a problem. However, a good deal of further research should be done in order to make the process practical. Given the expertise available at the Naval Research Laboratory and sufficient resources, we expect to accomplish these goals.

References

(1) N. C. Cook, "Metalliding", Scientific American 222, 38 (1969)

(2) e.g. "International Conference on Chemical Vapor Deposition", John M. Blocher, Jr., ed., Los Angeles, The Electrochemical Society, 1970

(3) Kosalopova, "Carbides", Plenum Press, New York, 1971

(4) G. Weiss, Ann Chim. [12], 1, 424 (1946)

(5) S. Senderoff and G. W. Mellors, Science 153, 1475 (1966)

(6) H. E. Bartlett and K. E. Johnson, Canad. J. Chem. 44, 2119 (1966)